

## 1,2-Bis-perfluoroalkylations of Alkenes and Alkynes with Perfluorocarboxylic Anhydrides

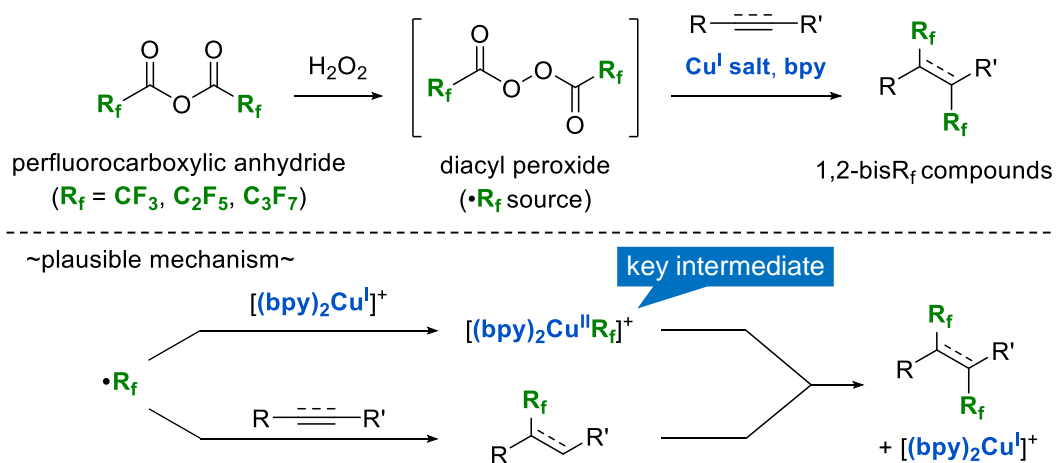
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**Keywords:** Perfluoroalkylation; Perfluorocarboxylic anhydrides; Diacyl peroxides; Perfluoroalkyl radicals; Organocopper intermediates

Perfluoroalkyl-containing organic molecules are of interest as pharmaceuticals and organic functional materials because of their improved physical, chemical, and biological properties derived from their fluorine atoms. Among perfluoroalkyl molecules, alkanes and alkenes bearing two perfluoroalkyl groups on their vicinal carbons are expected to exhibit unique functions; thus methods toward the 1,2-bis-perfluoroalkylation of alkenes and alkynes have been actively studied for nearly 50 years. Whereas various 1,2-bis-trifluoromethylations have been well established by using sophisticated trifluoromethylating reagents in the last decade, 1,2-bis-perfluoroalkylations that can introduce long perfluoroalkyl chains still have room for improvement due to the limitation of perfluoroalkylating reagents.

We developed the Cu-mediated 1,2-bis-perfluoroalkylation of alkenes and alkynes by using inexpensive and readily available perfluorocarboxylic anhydrides.<sup>1</sup> Diacyl peroxides were generated in situ from the carboxylic anhydride and hydrogen peroxide, which are served as a perfluoroalkyl radical source ( $\bullet R_f$ ). The reaction allowed us to obtain various 1,2-bis-perfluoroalkylated compounds including unique tetrasubstituted alkenes. Addition of bipyridyl ligand was found to improve the product yield. Our mechanistic studies suggested that the key step in this reaction should be the formation of a stable perfluoroalkylcopper intermediate  $[(bpy)_2Cu^{II}R_f]^+$  with the aid of a bipyridyl ligand; the intermediate plays the role in introducing the second perfluoroalkyl group to the alkyl- or vinyl-radical generated by the reaction of the substrate alkene or alkyne with perfluoroalkyl radical.



1) T. Tagami, Y. Aoki, S. Kawamura, M. Sodeoka, *Org. Biomol. Chem.* **2021**, *19*, 9148.